Production and transport of denitrification gases in shallow ground water

R. Well[1], J. Augustin[2], J. Davis[3], S.M. Griffith[4], K. Meyer[5] & D.D. Myrold[3]

[1]*Institut für Bodenwissenschaft, Von-Siebold-Str.4, 37075 Göttingen, Germany;* [2]*Institut für Primärproduktion und Mikrobielle Ökologie Zentrum für Agrarlandschaftsforschung (ZALF e.V.), Eberswalder Str. 84, 15374 Müncheberg, Germany;* [3]*Department of Crop and Soil Science, Oregon State University, Agricultural and Life Sciences Building 3017, Corvallis, OR 97331-7306, USA;* [4]*USDA-ARS National Forage Seed Production Res. Center, Corvallis, OR, USA;* [5]*Geries-Ingenieure Büro für Standorterkundung, Weender Str. 87, 37073 Göttingen, Germany*

Abstract

The contribution of potentially intense denitrification in the saturated zone of hydromorphic soils to atmospheric N_2O levels is poorly understood because few data exist on shallow ground water N_2O production, consumption and transport to the atmosphere. The objective of the present study was to investigate the contribution of the saturated zone to surface N_2O emission for two fen soils and a Gleyic Luvisol with ground water tables at the surface during the experimental period. Total denitrification, denitrifier N_2O production, ground water dissolved N_2 and/or N_2O, and surface N_2O emissions were measured in situ. Concentrations of dissolved gases and surface emissions were also simulated with a simple process-based model assuming measured rates of N_2 and N_2O production or constant profiles of dissolved N_2O concentration. NO_3^- and N_2O were abundant in all samples of the three sites. Substantial N_2O surface emission originating from the saturated zone was measured at both fen sites. Total denitrification ranged from 0.9 to 1.58 mg N l^{-1} day^{-1} in the 15 – 35-cm layer of the fen soils and from 0.005 to 0.13 mg N l^{-1} day^{-1} in the 50 – 100-cm layer of the Gleyic Luvisol. The ratio of N_2O production to total denitrification ranged from 0.07 to 0.32 in the fen soils and from 0.06 to 0.08 in the Gleyic Luvisol. The ratio of N_2O production to total denitrification ranged from 0.07 to 0.32, and from 0.06 to 0.08, respectively. Concentrations of dissolved N_2O measured at the fen sites were 1 to 2 orders of magnitude lower than simulated concentrations. In contrast, measured N_2O emissions were within the order of magnitude of emissions simulated assuming measured N_2 and N_2O production rates. The agreement between measured and simulated N_2O concentrations and surface emissions was satisfactory when gas diffusivity was multiplied by 10 and N_2O reduction rate was multiplied by 20 in the simulation. Simulation of diffusive N_2O emission assuming constant values of measured N_2O concentration profiles resulted in emissions approximately one order of magnitude lower than the measured values. At the Lake Creek site, the measured peak concentration of dissolved N_2 and the concentration simulated assuming measured values of N_2 production were relatively close with values of 2.4 and 3.5 times the atmospheric equilibrium concentration, respectively. It was concluded that the disagreements between measured and simulated values of N_2O concentrations and emissions resulted from the underestimation of model parameters for gas transfer and/or for N_2O reduction to N_2, which were not measured. Future modeling attempts should include use of measured values for all model parameters to obtain a more realistic description of the dynamics of N_2O emission from the saturated zone.

Introduction

In the shallow ground water of lowlands and riparian areas, redox conditions are often favorable for intense denitrification processes (Ross, 1995). N_2O is an obligate intermediate product of biological denitrification and can either be emitted to the atmosphere or further reduced to N_2. The significance of soil denitrification for the global N_2O budget is governed by the N_2O:N_2 ratio of gaseous denitrification products
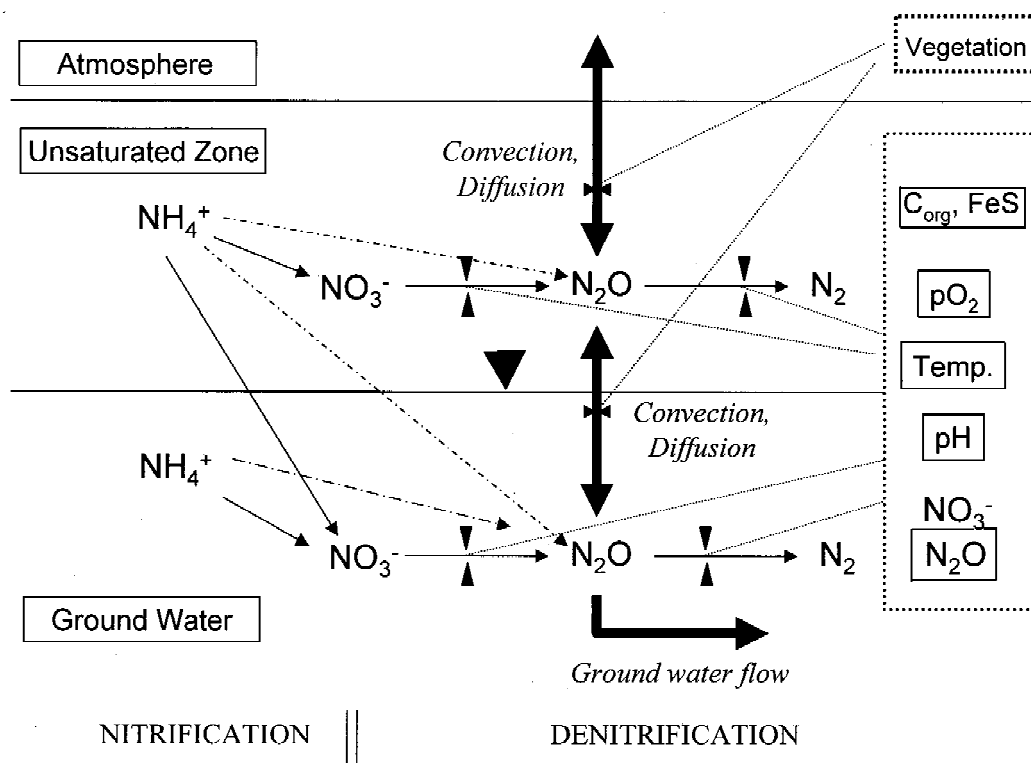
Figure 1. Conceptual model of N_2O turnover at the interface between the saturated zone and the atmosphere.

emitted at the soil surface, which is complexly controlled by a variety of soil parameters (Van Cleemput, 1998). The contribution of denitrification in the saturated zone to atmospheric N_2O levels depends on the rates of production and consumption, and of convective or diffusive transport (Figure 1). The current knowledge on the significance of the saturated zone as a source of atmospheric N_2O is still unsatisfactory (Groffman et al., 1998). Although numerous studies prove rapid NO_3^- consumption by denitrification in shallow ground water, the contribution to surface N_2O emission is still poorly understood. The potential for intense N_2O emission from hydromorphic soils is relatively well documented for fens (Augustin et al., 1998), whereas few emission data exist for riparian areas (Weller et al., 1994). None of these studies quantifies the relative contributions of the unsaturated and saturated zones to surface emission. Although there is a growing database on N_2O dissolved in ground water (Heincke & Kaupenjohann, 1999), little is known about its transfer to the atmosphere. Qualitative estimates of N_2O production and consumption in aquifers have been derived indirectly from the spatial distribution of N_2O and NO_3^- (Mühlherr & Hiscock, 1998;

Smith et al., 1991; Ueda et al., 1993). A few studies have directly measured N_2O production in the saturated zone using the ^{15}N tracer and acetylene block techniques (Jacinthe et al., 1998; Kliewer & Gilliam, 1995; Smith et al. 1996; Well et al., 2000). Significant N_2O emission from the subsoil to the atmosphere can be promoted by plants through rapid diffusive gas transport in the aerenchyma of wetland plants (Augustin et al., 1999; Stengel et al., 1987) and convective transport of dissolved gases during transpiration of plants without aerenchyma (Chang et al., 1998). To quantify the contribution of shallow ground water denitrification to atmospheric N_2O at a specific site it was necessary to take all of the N_2O turnover processes into account (see Figure 1). To our knowledge this has not yet been experimentally realized.

The growing evidence of agriculture's contribution to global atmospheric N_2O levels has promoted various attempts to predict soil N_2O emission. The existing process-based trace gas simulation models (Frolking et al., 1998) do not yet include subsoil denitrification processes. The OECD/IPCC/IEA II methodology for estimating N_2O emission from agricultural soils (Mosier et al., 1998), uses empirical N_2O emis-

sion factors and distinguishes direct soil emissions and indirect emissions from leached nitrogen. This method assumes that a constant fraction (0.025) of the nitrogen leached from the topsoil is emitted to the atmosphere as N_2O. However, none of the current methodologies considers the variability of subsoil properties controlling the reduction of NO_3^- and the production or consumption of N_2O by denitrification.

The objective of the present study was to investigate the contribution of the saturated zone to surface N_2O emission for three hydromorphic soils. We attempted to include all of the major processes contributing to surface emission (see Figure 1). Sites with continuous measurements of surface N_2O emission and/or shallow ground water dissolved N_2O were selected for the investigation. Total denitrification and N_2O production were measured in situ. Experiments were conducted during periods when the level was at the surface to exclude the uncertainty of unknown process rates in the unsaturated zone. Transfer to the atmosphere was simulated using a simple process-based model.

Material and methods

Field studies

A description of the experimental sites is given in Table 1. Ground water tables were at the surface during all experiments.

Surface N_2O emission was determined weekly during several years at the Müncheberg and Dümmer sites using the closed chamber method (Augustin et al., 1997; Meyer et al., 1997).

Ground water dissolved gases were measured at two of the sites. At the Dümmer site, non-convective gas collection probes (Schack-Kirchner et al., 1993) consisting of a 2-mm ID stainless steel tube with a perforated 8-cm bottom section and a hypodermic needle at the top were installed with four replicates at 10, 20, 30, 40 and 50 cm depth. Gas samples were collected weekly by attaching a helium-flushed Vacutainer for a period of 7 days. Then the gas samples were analyzed for N_2O. From the absence of helium in the gas samples it was concluded that the sampling period was sufficient to obtain an equilibrium between the soil water dissolved gas and the Vacutainer gas (Meyer, 1999). The Lake Creek site was instrumented with closed headspace wells that consisted of 5 cm diameter, 20-cm long PVC with screening intervals at 30

– 45 and 135 – 150 cm depth. The wells were sealed at the top except for 3.2 mm tubing that extended to the surface of the soil for sampling. Samples were collected biweekly by slowly pulling soil solution into a syringe and injecting it into an evacuated vial. A helium headspace was created in the vials, equilibrated with the water, and gas samples were analyzed for N_2O, N_2 and Ar. Dissolved gas concentrations were calculated using Henry's law.

Denitrifier N_2 and N_2O production was measured at all sites using an in situ injection-extraction method for water-saturated soils (Figure 2; Well & Myrold, 1999; Well et al., 2000). This procedure was based on the ^{15}N tracer and acetylene block techniques to detect gaseous denitrification products. Test solutions containing ^{15}N-labeled or unlabeled NO_3^- with or without acetylene were applied to the water-saturated soil. Subsequently, soil solution samples were collected during 2 days and dissolved denitrification products are measured to quantify N_2O production and total denitrification. Two types of subsoil probes (A and B) were used to inject and extract test solutions at 15 and 35 cm depth (Müncheberg and Dümmer sites), or at 50, 75 and 100 cm depth (Lake Creek). Both types of probes consisted of a filtering surface at the bottom, a Luerlock mini-valve with a hypodermic needle at the top for sample collection, and PE-tubing surrounded by a solid pipe to connect top and bottom. Type A probes (stainless steel, 1 cm OD) were used for the fen soils and were installed by pushing them into the soil. Type B probes (PVC, 5 cm OD) were equipped with an inflatable rubber gasket to prevent preferential flow to the surface and were used for the mineral soil (Lake Creek). The probes of each experiment were positioned in two rows with 1-m distances between and within the rows. The number of replicate probes per depth was twelve (Dümmer experiment) or eight (other experiments). In each experiment, one-half of the probes received solutions containing 50 ml l^{-1} acetylene to block the reduction of N_2O to N_2, allowing the estimation of total denitrification from the concentrations of dissolved N_2O. The other half received solutions without acetylene to determine soil N_2O production. Test solutions also contained 20 mg NO_3^--N l^{-1} (Dümmer experiment) or 10 mg NO_3^--N l^{-1}(other experiments). ^{15}N-NO_3^- (74 atom% ^{15}N) was used to allow the detection of gaseous denitrification products by isotope analysis. In the treatments without acetylene, the $^{15}N_2O$:$^{15}(N_2+N_2O)$ ratio represents the N_2O fraction of total denitrification products. In the

Table 1. Experimental sites and basic soil properties

Location	Soil	Land use	Depth of in situ experiments (cm)	Date of in situ experiments	Substrate	pH (CaCl$_2$)	Porosity (v/v)	C_{org} (%)
Dümmer, Lower Saxony, Northwest Germany	Acid fen, moderately degraded	Grass, rewetting experiment	15	6 Dec. 1997	Peat	4.7	0.76	24.30
			35		Peat	4.7	0.81	50.70
Müncheberg, Brandenburg, Northeast Germany	Fen, weakly degraded	Alder (*Alnus glutinosa*) forest	15	3 – 5 Nov. 1998	Peat	5.7	0.87	39.50
			35		Peat	5.7	0.92	41.60
Lake Creek, Western Oregon, USA	Gleyic Luvisol	Grass seed (*Lolium perenne*)	50	2 – 4 March 1999	Silt loam	5.0	0.43	0.51
			75		Silt loam	5.2	0.38	0.3
			100		Silt loam	5.5	0.45	0.14

acetylene treatments, total dissolved ^{15}N equals dissolved N$_2$O, provided the N$_2$O reductase is completely blocked. The ^{15}N$_2$O:^{15}(N$_2$+N$_2$O) ratio indicates if the blockage is complete. Therefore, the use of ^{15}N in the treatments with acetylene is a tool to check the method, but is dispensable for the determination of denitrification rates. To reduce experimental costs, only one out of four replicates of the acetylene treatments of the Müncheberg and Lake Creek experiments received ^{15}N. At these sites, 100 mg l^{-1} Cl$^-$ (Müncheberg) or Br$^-$ (Lake Creek) were added to the test solutions as KCl or KBr, respectively. Thus, it was possible to determine the mixing ratio of test solution and original soil solution in the samples collected following the injections from Cl$^-$ or Br$^-$ concentrations. Test solutions were prepared in flexible hot water bottles (2 l) (Müncheberg, Dümmer) or 20-l flexible water carriers (Lake Creek) to prevent contact with the atmosphere. Soil solution samples were collected by attaching evacuated serum bottles (50 or 100 ml, 50 or 75 kPa vacuum) sealed with crimp-caps and rubber septa to the subsoil probes by inserting the hypodermic needle through the rubber septa. At the beginning of each experiment, a sample was collected from each probe to determine background values of NO$_3^-$, Cl$^-$, and dissolved N$_2$O. Subsequently, 4 l (Müncheberg, Dümmer) or 16 l (Lake Creek) of test solution were applied to each probe via gravity. To increase the gravity gradient, the bottles with the test solutions were placed 50 cm (Dümmer experiment) or 150 cm (other experiments) above ground. After the injection, water samples (one per probe and sampling event) were collected at 2-h intervals during 8 h (Dümmer experiment) or at 8-h intervals during 2 days (other

experiments). One gas sample from the headspace of each soil solution sample was transferred to an evacuated 10-ml vial. Soil solutions were analyzed for Cl$^-$ or Br-, and NO$_3^-$. Gas samples were analyzed for N$_2$O, ^{15}N$_2$, ^{15}N$_2$O and C$_2$H$_2$. Dissolved gas concentrations were calculated using Henry's law. N$_2$ and N$_2$O production rates were determined from the time course of dissolved gas concentrations.

^{15}N$_2$ and ^{15}N$_2$O were analyzed with an elemental analyzer (ANA 1400, Carlo Erba, Milano) coupled to a dual inlet, isotope ratio mass spectrometer (MAT 251, Finnigan, Bremen) as described earlier (Well & Myrold, 1999). N$_2$O and analysis was conducted with a gas chromatograph (Fractovap 4200, Carlo-Erba, Milano) equipped with an electron capture detector (ECD 400, Carlo-Erba, Milano) and using Argon-Methane (95:5) as carrier. N$_2$ and Ar were measured with a gas chromatograph equipped with a thermal conductivity detector (Carle Series 100 AGC, Loveland). NO$_3^-$ was measured by steam distillation (Bremner and Keeney, 1965). Cl$^-$ was determined with a titroprocessor (626, Metrohm, Herisau), and Br$^-$ with a continous flow analyzer (Lachet, Milwaukee).

The ^{15}N data proved, that the blockage of N$_2$O reductase in the presence of acetylene was complete, and that the ratio of N$_2$O production rates from probes treated with and without acetylene was a reliable estimate of the N$_2$O/(N$_2$+N$_2$O) ratio of gaseous denitrification products (Well et al., 2001). The rates of denitrification and N$_2$O production presented in this study are exclusively based on the N$_2$O measurements.

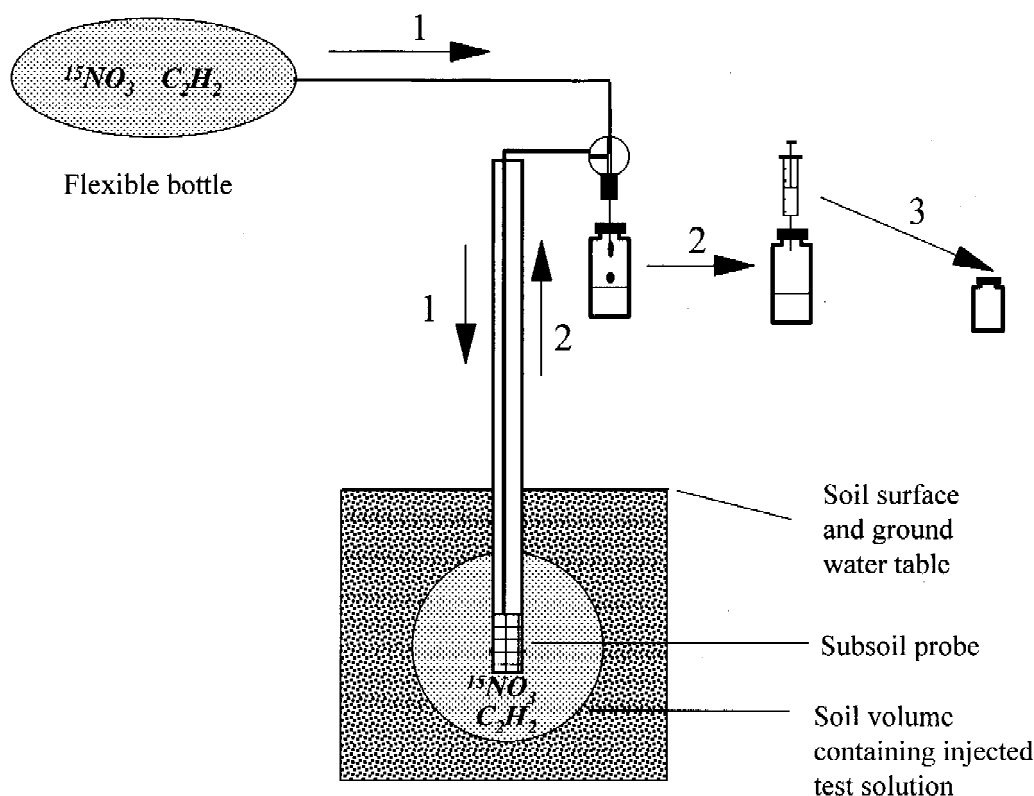Background concentrations of gaseous denitrification products in the saturated zone were determined

Figure 2. Experimental setup for in situ measurement of denitrifier N_2 and N_2O production. Path 1: injection of test solution into the saturated zone. Path 2: sampling of soil solution with pre-evacuated serum bottles. Path 3: sampling of equilibrated headspace gas for subsequent analysis of gaseous denitrification products.

using the initial samples of the injection experiments (Müncheberg and Lake Creek sites), or from non-convective gas collection probes (Dümmer site).

The injection/extraction experiments at the fen sites were both conducted in late fall (Table 1) approximately 2 weeks after the rising of the water table to the soil surface. During this period NO_3^- is present which originated from nitrification processes under the preceding unsaturated phase. During saturation, NO_3^- disappeared within a few weeks, presumably as a result of intense denitrification. Injection/extraction experiments were conducted at the Lake Creek site during late winter, approximately 2 – 3 months after initial saturation of the topsoil. At this site, the ground water table is close to the surface during the entire wet season between November and April. NO_3^- concentrations rarely dropped to zero in the shallow ground water, apparently because denitrification activity was not sufficient for complete removal of the nitrogen surplus from fertilizer applications.

Simulations

The objectives of simulating the investigated systems were twofold. For the fens we intended to simulate N_2O exchange between the saturated zone and the atmosphere. The quality of the simulations was limited by the fact that experimental data were not available for some of the model parameters. Therefore, we did not expect to obtain a quantitative fit of measured and simulated data. The aim of this simulation was to evaluate if N_2O production in the saturated zone of the experimental sites is a probable explanation for the measured surface emissions of N_2O. The idea of the Lake Creek simulation was to test the model with an additional gas species. Here, we compared simulated N_2 concentrations based on measured N_2 production rates with measured N_2 concentrations. We expected this simulation to be more accurate, because some of the uncertain model parameters of the N_2O simulation (e.g. N_2O reduction to N_2, N_2O production during nitrification) have a minor effect on N_2 production. Thus, the comparison of the two simulations might

reveal weaknesses in the model that apply only to N_2O.

For simulating production, consumption and transport of denitrification gases, a one-dimensional finite-difference model for gas production/diffusion in soil (Anlauf et al., 1990) was used that is based on the following numerical solution of Fick's second law of diffusion:

$$C_{i,j+dt} = C_{i,j} + \Delta t (D_a/\epsilon)[A_i(C_{i-1} - C_i)/$$
$$\Delta z - A_{i+1}(C_i - C_{i+1})/\Delta z]/V_i + P_i - R_i$$

where i is the variable of locality, j is the variable of time, C is the gas concentration, Δt is the time interval, ϵ is the porosity, D_a is the apparent gas diffusion coefficient, Δz is the distance interval, A is the cross-section area of cells, V is the volume of the cells, P is the gas production rate, and R is the rate of N_2O reduction to N_2. Gas diffusivity in the water filled pore space is given by the gas diffusion coefficient in water (2.03×10^{-5} cm^2 s^{-1} at 20°C) and the tortuosity of the soil pores. A tortuosity of 1.5 was assumed for the fen soils. This value was chosen because the porosity of the fens was high compared to most mineral soils which typically have a tortuosity of 2.7 (Frede, 1986). The simulated vertical soil column was 100 cm in depth with 5-cm intervals. The lower boundary was defined as an impermeable layer ($D_a = 0$). The impact of this simplification was evaluated in earlier simulations with a lower boundary deeper than 100 cm. Results showed that downward diffusion has a minor effect on simulated concentrations above 100 cm. The upper boundary was defined to be constantly at ambient N_2O concentration (0.3 ppm). Surface emission was derived from diffusion across the upper boundary. Convective transport of dissolved gas was assumed to be zero. The following two different types of simulations were conducted.

(A) Simulation of surface N_2O emission and ground water N_2O concentration assuming measured production rates (fen sites)

The objective was to evaluate the agreement of measured surface emissions and ground water concentrations to values that were simulated using measured productions rates. The 20-day simulation period was intended to represent the phase of rapid consumption of residual NO_3^-. Production of (N_2+N_2O) and the $N_2O{:}(N_2+N_2O)$-ratio were assumed to be directly related to NO_3^- concentration. Initial NO_3^- concentrations were set to 10 mg N l^{-1}; production of (N_2+N_2O) and the $N_2O{:}(N_2+N_2O)$-ratio were set according to the measured data. NO_3^- reduction was set equal to the $N_2 + N_2O$ production rate. For estimating the N_2O reduction rate it was assumed that dissolved NO_3^- and N_2O would be equal substrates for the denitrifying population. Thus, the N_2O reduction rate was calculated as $R = DR \times C_{N_2O}/C_{NO_3+N_2O}$, where DR is the measured total denitrification rate, and $C_{N_2O}/C_{NO_3+N_2O}$ is the ratio of N_2O to NO_3^- plus N_2O in the soil solution.

(B) Simulation of steady state surface emission assuming constancy of the measured concentration profiles (fen sites)

The objective was to determine if measured N_2O surface emission can be explained by diffusive flux of N_2O that was dissolved in the ground water. In this simulation, the measured concentration profiles were assumed to be constant. Concentration profiles were constructed by interpolating the measured N_2O concentrations. Production and consumption were set to zero. Simulation time was continued until constant emissions were obtained.

(C) Simulation of dissolved N_2 concentration and surface N_2 emission assuming measured N_2 production rates (Lake Creek site)

A period of 100 days was simulated in order to describe the phase from initial water saturation until the occurrence of maximum concentrations of dissolved N_2. A 0 – 100 cm profile of N_2 production was determined by interpolating rates between 50 and 100 cm and by assuming that the 50 cm value was also valid for the soil between 0 and 50 cm depth. Because NO_3^- was permanently present during saturated conditions, N_2 production was assumed to be constant. N_2O production and N_2O reduction to N_2 were not simulated. Initial dissolved N_2 concentrations were set to the atmospheric equilibrium values.

Results and discussion

Injection experiments

Intense denitrification was observed in the 15 – 35-cm layer of the fen soils with total denitrification rates ranging between 900 and 1580 μg N l^{-1} day^{-1} (Table 2). The mineral soil yielded lower rates that decreased from 130 μg N l^{-1}day^{-1} at 50 cm to 5 mg N l^{-1}day^{-1} at 100 cm. This pattern is in agreement with earlier studies reporting intense denitrification in the presence

Table 2. Total denitrification rates, N_2O fractions of total denitrification, concentrations of dissolved N_2O, N_2O emission at the soil surface (simulated concentrations and emissions). Means $\pm$ standard deviations from four replicate probes or six replicate soil covers (N_2O emission studies)

Site	Depth (cm)	NO_3^- conc. (mg N l^{-1})	Denitrification Rate (μg N l^{-1} day^{-1})	N_2O Fraction[1]	N_2O concentration (μg N l^{-1})		N_2O Emission (g N ha^{-1} day^{-1})		
					Measured	Simulated A[2]	Measured	Simulated A[2]	Simulated B[2]
Dümmer	Surface						26.2 ± 16.2	41.3	0.7
	15	3.1 ± 2.0	900 ± 610	0.22	16.5 ± 21.0	1103			
	35		1020 ± 410	0.31	71.4 ± 82.0	1110			
Müncheberg	Surface						66.6 ± 22.9	22.0	0.2
	10	9.6 ± 7.6	1580 ± 670	0.07	10.2 ± 16.6	527			
	30	20.5 ± 6.7	1080 ± 550	0.10	56.3 ± 45.8	527			
Lake Creek	50	8.4	130 ± 190	0.08	6.5 ± 2.7				
	75	11.1	7 ± 6	0.07	8.9 ± 1.4				
	100	8.6	5 ± 7	0.06	6.6 ± 1.9				

[1] Ratio of N_2O production without acetylene to N_2O production with acetylene.
[2] *A*, maximum values of a 20-day-simulation using measured N_2O production rates; B: steady state values of a simulation assuming the measured concentration gradients to be constant with time.

of high availability of organic carbon in organic horizons (Augustin et al., 1997; Terry & Tate, 1980) or C-limitation of denitrification increasing with depth in mineral soils (Rice & Rogers, 1993).

The N_2O fraction of total denitrification products was higher in the acid fen (0.22 – 0.31) compared to the other soils (0.06 – 0.10). This finding is in agreement with the known inhibition of N_2O reductase under acid conditions (Blackmer & Bremner, 1978; Firestone et al., 1980).

Ground water dissolved N_2O and NO_3^-

At each site both NO_3^- and N_2O were abundant in all investigated layers (Table 2). The substantial surface emissions of N_2O measured at both sites originated from the saturated zone because the ground water table was at the surface during the measurements.

Comparison of measured ground water N_2O concentrations and surface emissions with simulated data (fen sites)

Simulation A (Fig. 3a,b) predicts an initial phase of steep increase followed by a phase of gradual decrease of both ground water N_2O concentration and surface emission. Because initial concentrations are at atmospheric equilibrium and production is at a maximum the initial phase is dominated by accumulation. Concentrations and emissions decrease in the second phase as a result of decreasing NO_3^- concentration and thus decreasing production and increasing N_2O reduction to N_2. The maximum concentrations and emission rates of the simulations were selected for comparison with the measured values (Table 2). We chose these values because we assumed that denitrification was not NO_3^- limited in either of the two fen sites during the field measurement of surface emission and initial ground water N_2O concentration. This simplification was necessary because the relationship between NO_3^- concentration and denitrification rate was not determined experimentally. Measured concentrations were 1 – 2 orders of magnitude lower than simulated concentrations, whereas measured emissions were in the order of magnitude of maximum emissions of simulation A. From these observations it can be concluded that the model parameters that were chosen for gas transfer, N_2O reduction to N_2, or both, were much lower than the true values. Simulation of diffusive emission assuming constant values of measured concentration profiles (simulation B) results in emissions approximately one order of magnitude lower than the measured values. These results indicate, that the true rate of gas transfer was higher than the diffusive flux that was determined with the simulations.

In the following, various possible explanations for the discrepancy between simulated and measured data are discussed. One question is if the measured values of model parameters were representative for the
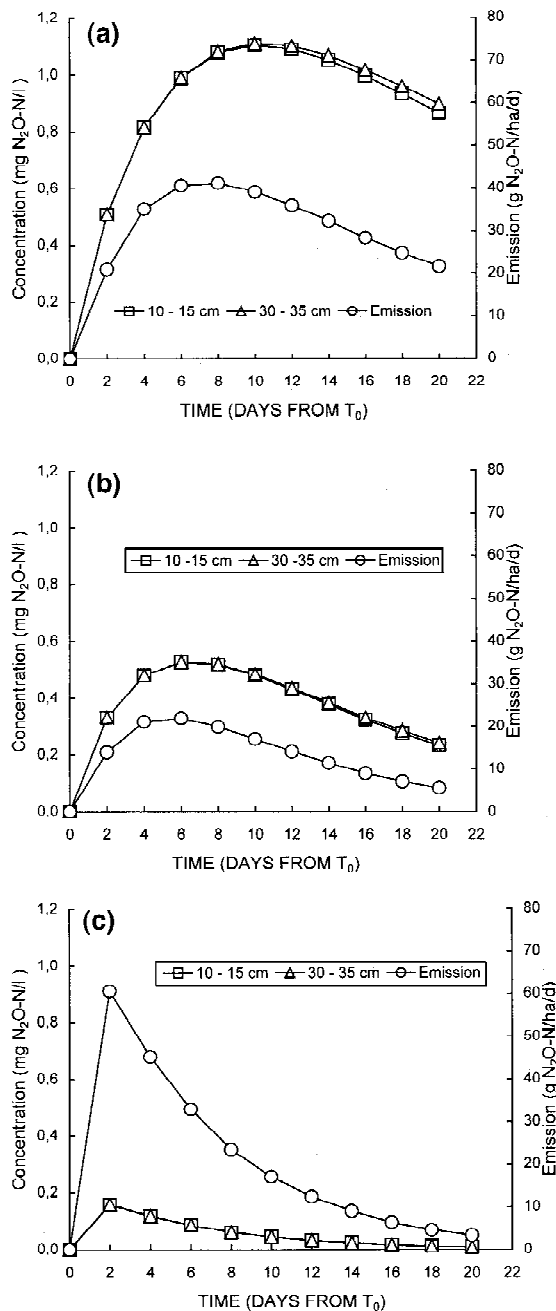
Figure 3. (a) Simulated N_2O concentration and surface emission (Müncheberg site). (b) Simulated N_2O concentration and surface emission (Dümmer site) (c) Simulated N_2O concentration and surface emission assuming increased values of diffusivity ($10 \times D_a$) and N_2O reduction to N_2 ($20 \times R$) (Dümmer site).

sites during the simulated period. Although soil denitrification is known to be highly variable in space and time we assumed that the data measured during a single experiment per site were a reasonable estimate of the processes during the simulated periods, because the soils were permanently waterlogged and the variation in soil temperature is typically low during late fall. This is supported by the narrow range of the measured denitrification rates in the fen sites (Table 2). Gas transfer may have been underestimated either because the estimation of the diffusion coefficients were inaccurate or because transport processes other than liquid phase diffusion had a significant contribution to gas transport. Tortuosity is the principal factor controlling gas diffusivity in a water saturated matrix. The tortuosity factor of 1.5 is relatively close to the minimum value of 1 which applies to non-tortuous pores. Therefore, underestimation of liquid phase diffusion could explain only a minor part of the observed discrepancies. Lateral convective transport could theoretically explain the discrepancy between measured and simulated concentrations, because it would reduce accumulation of N_2O produced in the saturated zone. However, it would not explain the underestimation of true emissions by simulation B. Furthermore, significant convective transport is unlikely for the Dümmer site, because precipitation was negligible during the preceding week and because the site was part of a re-wetting experiment in which drainage was artificially inhibited (Meyer, 1999). At the Müncheberg site it was possible that lateral flow exported a certain fraction of the N_2O load from the swamp site to a bordering lake. The extent of this path cannot be quantified because hydrological data were not available.

Plants could be a possible explanation for accelerated gas transfer through high gas diffusivity in the aerenchyma of certain wetland grasses (Augustin et al., 1999) or black alder trees (*Alnus glutinosa*; Rusch & Rennenberg, 1998), or convective flow during transpiration in plants without aerenchyma (Chang et al., 1998). Grass species with aerenchyma, such as *Phragmites*, were rare at both fen sites, but there may have been N_2O transport through the alder trees that were present at the Müncheberg site. However, tree flux did not contribute to the measured surface flux, because the measurements were conducted with chambers that did not include the trees. At the measured soil water concentrations of N_2O, plant transpiration could explain emissions between 0.39 and 0.56 g N_2O-N ha^{-1} day^{-1} per mm of transpiration. Experiments were conducted during November and December, when

potential evapotranspiration in Northern Germany is generally below 1 mm day^{-1} (Keller, 1978), thus transpiration can explain only a minor fraction of the measured emissions.

N$_2$O production during nitrification was not considered in the model because this path had been assumed to be insignificant in the investigated systems. In the fen sites, conditions were not favourable for nitrification due to water-saturation and low soil temperatures (Dümmer: 3°C at 15 cm depth; Müncheberg: 7°C at 10 cm depth). For the Dümmer site, potential N$_2$O production during nitrification can be estimated from in situ measurements of C-mineralisation (Meyer, 1999). Mineralisation rates measured during November and December ranged between 1.6 and 3.1 kg C ha^{-1} day^{-1}. This corresponds to a potential N$_2$O production of 1.1 – 2.2 g N ha^{-1} day^{-1} if a C:N ratio of 14 (Meyer, 1999) and a maximum N$_2$O:NO$_3$ ratio of 1% (Hutchinson & Davidson, 1993) is assumed. Thus, nitrification could explain only a small fraction (less than 10%) of the N$_2$O-emission measured at the Dümmer site. We expect that the same was valid for the Müncheberg site, because temperature and moisture conditions were similar.

Underestimation of the rate of N$_2$O reduction to N$_2$ could be one possible explanation for overestimation of ground water N$_2$O concentrations in the simulations. We assumed that the denitrifying population had the same affinity to NO$_3^-$ and to N$_2$O. One reason for a preferred N$_2$O reduction would be the fact that many denitrifiers are not able to perform all the steps of the denitrification process (Knowles, 1982). Denitrifiers with the capability to reduce only N$_2$O to N$_2$ are known, although they were found less frequently compared to species lacking N$_2$O reductase. Nevertheless, if such denitrifiers were present, they would reduce N$_2$O independently of the N$_2$O:(N$_2$O+NO$_3^-$)-ratio and thus contribute to a preferred consumption of N$_2$O.

Additional simulations were conducted to improve the fit of simulated and measured values by increasing gas diffusivity and/or N$_2$O reduction. By increasing only one of the quantities, it was not possible to fit both emission and concentration. Fig. 3c shows the results of a simulation for the Dümmer site using increased values of diffusivity (10 × D_a) and N$_2$O reduction (20 × R). During the later part of the simulated time period simulated emission and concentrations are in the same order of magnitude as the measured values. Consequently, simultaneous underestimation of both
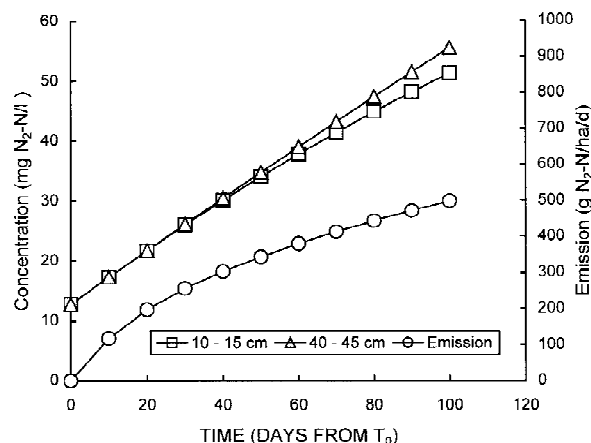

Figure 4. Simulated N$_2$ concentration and surface emission (Lake Creek site).

parameters is a possible explanation for the poor fit of the initial simulations.

Comparison of measured and simulated ground water dissolved N$_2$ (Lake Creek site)

Measurement of N$_2$:Ar ratios in the 30 – 45-cm piezometers began on 16 February 1999, approximately 12 weeks after initial water saturation of the top soil. The values were highest on the first sampling date with a value of 60.6 ± 3.5, which is 2.4 times the atmospheric equilibrium ratio. Ratios gradually decreased during the remaining wet period. The simulation (Figure 4) predicts an almost linear increase of dissolved N$_2$ concentration at 40 cm depth during the saturated period. Twelve weeks after the beginning of the simulation the concentration was 3.5 times the atmospheric equilibrium value (initial concentration). At this first sampling event measured and simulated concentrations agree relatively well. However, simulations predict a further increase of the N$_2$:Ar ratio and the measurements exhibited a decrease of ratios (data not shown). The agreement between measured and simulated N$_2$ concentrations is much better compared to the dissolved N$_2$O concentrations in the fen simulations, where the discrepancy was more than one order of magnitude. One of the main limitations of the fen simulations was the uncertain estimation of N$_2$O reduction to N$_2$. This process was neglected in the Lake Creek simulations, which was an appropriate simplification because N$_2$O production rates were below 8% of total denitrification (Table 2). Accelerated gas transfer through plants was probably not important at Lake Creek, because aerenchymous plants were not

present and evapotranspiration was low during winter. The assumption of constant denitrification rates in 0 – 50 cm depth is a potential source of error because potential denitrification in mineral soils is generally highest in the top layer. To evaluate this, the impact of tripling the denitrification rate in the 0 – 30 cm layer on dissolved N_2 concentration at 40 cm depth was tested in a simulation (data not shown). These simulated N_2 concentrations at 40 cm depth were less than 10% higher compared to the N_2 concentrations in Figure 4.

Entrapped air, which is frequently found in shallow ground water (Fayer & Hillel, 1986), increases the amount of atmospheric N_2 and Ar in the saturated soil column and therefore affects the relationship between N_2 production from denitrification and ground water N_2:Ar ratio. Lateral convective transport would lower the accumulation of dissolved N_2 and is known to play an important role at the Lake Creek site during the wet season (Horwath et al., 1998). Both parameters were not included in the simulation because quantitative data were not available.

Among the uncertain parameters entrapped air and lateral flow would have the strongest impact on dissolved N_2 concentration and would both have a decreasing effect. Therefore, the simulated dissolved N_2 concentration should be considered as a maximum of the range of possible values.

Conclusions

Significant production of N_2 and N_2O occurs in the saturated zone of hydromorphic experimental soils, resulting in accumulation of these gases in the ground water. In the fens, a certain fraction of N_2O is then emitted from the saturated zone directly to the atmosphere before further reduction to N_2 can occur. The quantities of N_2O production during denitrification, N_2O accumulation and N_2O emission, as directly determined simultaneously at the fen sites, are in disagreement with the results of model simulations, presumably because the model assumptions for N_2O transport and reduction to N_2 underestimated the true values. Measured and simulated N_2 production rates and dissolved N_2 concentrations of the Gleyic Luvisol agreed relatively well. These results demonstrate that process-based modeling is a promising tool to explain the linkage between shallow ground water production, accumulation and emission of N_2O. In order to obtain more accurate results, future modeling attempts have to be based on a more complete dataset including direct measurements of the uncertain model parameters and a higher spatial and temporal resolution.

References

Anlauf R, Kersebaum KC, Ping LY, Nuske-Schüler A, Richter J, Springob G, Syring KM & Utermann J (1990) Models for processes in the soil. Catena, Cremlingen, 227pp.

Augustin J, Merbach W, Käding H, Schmidt W, Schalitz G, Russow R & Ende HP (1997) N balance experiments on fen grassland with ^{15}N labeled fertilizer. Isotopes Environ Health Stud 33: 1–7.

Augustin J, Merbach W, Steffens L & Snelinski B (1998) Nitrous oxide fluxes of disturbed minerotrophic peatlands. Agribiol Res 1: 37–46.

Augustin J, Russow R & Münchmeyer U (1999) Effect of wetland plants on N transformation and gaseous N losses (N_2O, N_2) of degraded fen peatlands. Abstract 10th Nitrogen workshop, Royal Veterinary and Agricultural University Copenhagen, Denmark, August 23–26, 1999.

Blackmer AM & Bremner JM (1978) Inhibitory effect of nitrate on reduction of nitrous oxide to molecular nitrogen by microorganisms. Soil Biol Biochem 19: 187–191.

Chang C, Janzen HH, Cho CM & Nakonechny EM (1998): Nitrous oxide emissions through plants. Soil Sci Soc Am J 62: 35–38.

Fayer MJ & Hillel D (1986) Air encapsulation: I. Measurement in a Field Soil: Soil Sci Soc Am J 50: 568–572.

Firestone KK, Firestone RB & Tiedje JM (1980) Nitrous oxide from soil denitrification: factors controlling its biological production. Science 208: 749–751.

Frede G (1986) Der Gasaustausch des Bodens. Göttinger Bodenkundliche Berichte 87, 130pp (in German).

Frolking SE, Mosier AR, Ojima DS, Li C, Parton WJ, Potter CS, Priesack E, Stenger R, Haberbosch C, Dörsch P, Flessa H & Smith KA (1998) Comparison of N_2O emissions from soils at three temperate agricultural sites: simulations of year-around measurements by four models. Nutr Cycl Agroecosyst 52: 77—105.

Groffmann PM, Gold AJ & Jacinthe PA (1998) Nitrous oxide production in riparian zones and groundwater. Nutr Cycl Agroecosyst 52: 179–186.

Heincke M & Kaupenjohann M (1999) Effects of soil solution on the dynamics of N_2O emission: a review. Nutr Cycl Agroecosyst 55: 133–157.

Horwath WR, Elliott LF, Steiner JJ, Davis JH & Griffith SM (1998) Denitrification in cultivated and noncultivated riparian areas of grass cropping systems. J Environ Qual 27: 225–231.

Hutchinson GL & Davidson EA (1993) Processes for production and consumption of gaseous nitrogen oxides in soil. In: Agricultural ecosystem effects on trace gases and global climate change. ASA Special Publications no. 55, Am Soc Agronomy, Madison, WI, pp 79–93.

Jacinthe PA, Groffmann PM, Gold AJ & Mosier AR(1998) Patchiness in microbial transformations in groundwater in a riparean forest. J Environ Qual 27: 156–164.

Keller R (1978) Hydrologischer Atlas der Bundesrepublik Deutschland. Boldt-Verlag, Boppard, 68pp, (in German).

Kliewer BA & Gilliam JW (1995) Water table management effects on denitrification and nitrous oxide evolution. Soil Sci Soc Am J 59: 1694–1701.

Knowles R (1982) Denitrification. Microbiol. Rev. 46: 43–70.

Meyer K (1999) Die Flüsse der klimarelevanten Spurengase CO_2, CH_4 und N_2O eines norwestdeutschen Niedermoores unter dem Einfluß der Wiedervernässung. Göttinger Bodenkundliche Berichte 11: 1–134 (in German).

Meyer K, Höper H & Blankenburg J (1997) Influence of different re-wetting levels on the emission of nitrous oxide from a fen soil in northwest Germany. In: Becker KH & Wiesen P (eds) Proceedings of the 7th workshop on nitrous oxide emissions. Cologne, Germany, pp 312–326.

Mosier AR, Kroeze C, Nevison C, Oenema O, Seitzinger S & Van Cleemput O (1998) Closing the N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. Nutr Cycl Agroecosyst 52: 225–248.

Mühlherr IH & Hiscock KM (1998) Nitrous oxide production and consumption in British limestone aquifers. J Hydrol 211: 126–139.

Rice CW & Rogers KL (1993) Denitrification in subsurface environments: potential source for atmospheric nitrous oxide. In: Agricultural ecosystem effects on trace gases and global climate change. ASA Special Publications no. 55, pp 121–132, Am Soc Agronomy, Madison, WI.

Ross SM (1995) Overview of the hydrochemistry and solute processes in British wetlands. In: Hughes JMR & Heathwaite AL (eds) Hydrology and hydrochemistry of British wetlands, pp 133—182. Wiley, New York.

Rusch H & Rennenberg H (1998) Black alder (*Alnus glutinosa* (L.) Gaertn.) trees mediate methane and nitrous oxide emission from the soil to the atmosphere. Plant Soil 201: 1–7.

Schack-Kirchner H, Hildebrandt E E & Von Wilpert K (1993) Ein konvektionsfreies Sammelsystem für Bodenluft. Z. Planzenernaehr Bodenkd 156: 307–310.

Smith RL, Howes BL & Duff JH (1991) Denitrification in nitrate contaminted groundwater: Occurrence in steep vertical geochemical gradients. Geochim Cosmochim Acta 55: 1815–1825.

Smith RL, Garabedian SP & Brooks MH (1996) Comparison of denitrification activity measurements in ground water using soil cores and natural gradient tracer tests. Environ Sci Technol 30: 3448–3456.

Stengel E, Carduck W & Jebsen C (1987) Evidence for denitrification in artificial wetlands. In: Reddy K & Smith WH (eds) Aquatic plants for water treatment and resource recovery. Proceedings of the conference on research and application of aquatic plants for water treatment and ressource recovery. pp 543–550. Magnolia Publishing, Orlando, FL.

Terry RE & Tate RL (1980) Denitrification as a pathway for nitrate removal from organic soils. Soil Sci 129: 162–166.

Ueda S, Ogura N & Yoshinari T (1993) Accumulation of nitrous oxide in aerobic groundwaters. Water Res. 27: 1787—1792.

Van Cleemput O (1998) Subsoils: chemo- and biological denitrification, N_2O and N_2 emissions. Nutr Cycl Agroecosyst 52: 187–194.

Well R & Myrold DD (1999) Laboratory evaluation of a new method for in situ measurement of denitrification in water-saturated soils. Soil Biol Biochem 31: 1109–1119

Well R, Augustin J & Meyer K (2001) In situ measurement of denitrification and N_2O production in the saturated zone of three Eutric Histosols and of a Mollic Gleysol. In: Broll G, Merbach W & Pfeiffer EM (eds) Soil ecological processes in wetlands of Germany (in press).

Weller DE, Corell DL & Jordan TE (1994) Denitrification in riparian forests receiving agricultural discharges. In: Mitch WJ (ed) Global Wetlands: Old World and New, pp 117–131. Elsevier Science, Paris.